

## Characterization of Working Catalysts (Needle in a Haystack Catalysis)

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### Introduction

A key goal of catalysis research is to understand the relationship between the catalyst structure and performance. For example, experiments using single crystals and surface science techniques have helped establish that some crystal planes are more active and/or selective than others. Ultimately, fundamental structure-performance studies are intended to illuminate the operation of industrial catalysts and the nature of active sites on complex catalytic surfaces. However, a key problem in relating fundamental studies with real catalyst performance is the so called “pressure-materials gap” [1] between surface science experiments and research at industrial conditions.

The TAP reactor provides the opportunity to perform experiments on real catalysts at industrial conditions and at high vacuum conditions close to the surface science regime. This paper reports results of new experiments in which TAP experiments are performed using a single micron-sized particle surrounded by a bed of inert particles. Using a single particle has a number of unique advantages especially revealing relationships between catalyst structure and performance. In single particle experiments, non-uniformities in catalyst composition and temperature profiles within the reactor are eliminated. Also the single particle can be moved to different axial and radial positions and the influence of catalyst position on observed reaction characteristics can be explored. By changing the particle position, the length of the inert particle bed or the size of the inert particles the number of gas-surface collisions can be precisely controlled. Also, by using a single catalyst particle, the number of active sites on the catalyst can be more precisely quantified. Single particles can be single crystals, deposited films, or industrial catalysts. Experiments can be performed at both vacuum conditions and atmospheric pressures in sequence, and results between the two regimes can be directly compared.

### Materials and Methods

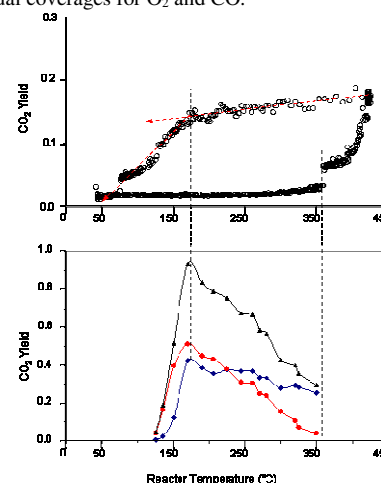
Single particle experiments were performed using the Temporal Analysis of Products (TAP-2) reactor system [2, 3]. Single catalyst particles were held in a stainless steel, cylindrical micro-reactor 4.19 cm in length and 0.64 cm in diameter. The reactor contains an internal thermocouple and a resistance heating system capable of 0.1° accuracy. Particles were obtained from a variety of sources including platinum foil, platinum powder, and platinum supported on alumina and silica. In this paper we report results using a 350  $\mu\text{m}$  diameter high-purity (99.9%) platinum powder particle packed in a bed of 100,000 inert quartz particles with diameters between 210–250  $\mu\text{m}$ . Atmospheric pressure and TAP vacuum pulse response experiments were performed at a variety of reactor temperatures. Atmospheric pressure experiments were conducted using stoichiometric mixtures of O<sub>2</sub> and CO (20 cc/min each) while ramping the reactor temperature up and down. Prior to performing TAP vacuum pulse response experiments, the catalyst was pre-treated by heating the particle in an oxygen flow. Subsequently, the catalyst was titrated using a series of alternating CO/Ar and O<sub>2</sub>/Ar pulses. This is known as a type of TAP pulse response experiment called the pump-probe method.

Typical pulse intensities used were on the order of  $1 \times 10^{14}$  molecules per pulse. Conversion in both TAP and normal flow conditions was determined as the ratio between the CO reacted to form CO<sub>2</sub> and the amount originally pulsed or flowed into the reactor. The

temperature dependence of CO conversion in the two regimes allowed the direct comparison of flow and TAP experiments over a wide range of operating conditions. Our estimates show that in both experiments, the temperature gradients within one particle are not significant.

### Results and Discussion

CO conversion is much higher under TAP vacuum conditions than atmospheric flow pressures. Under TAP conditions, a maximum in CO conversion of nearly 95% is observed at 170 °C. At this same temperature, a conversion of only 15% is obtained under atmospheric flow conditions. Interpretation of this difference is done based on the hydrodynamic characteristics of these two regimes. At 170 °C, this is the turning point in both pressure regimes where there is a transition in coverage of surface species from either a CO dominated state or an oxygen dominated state depending on the direction of temperature increase or decrease. In the region of the CO<sub>2</sub> yield maximum, the areas under the CO<sub>2</sub> response curves corresponding to the O<sub>2</sub> and CO pulses are approximately the same, indicating nearly equal coverages for O<sub>2</sub> and CO.



**Figure 1.** Comparison between CO<sub>2</sub> production observed under TAP atmospheric flow and vacuum conditions. A correlation at the “turning point” (170 °C) is observed for the two pressure regimes.

### Significance

Correspondence between characteristics observed in both vacuum and atmospheric pressure regimes (“turning points”, estimations of CO and O<sub>2</sub> surface coverages) indicate that the kinetic data obtained in vacuum experiments can be used to describe kinetic behavior in the atmospheric pressure domain. The ability to relate data in the atmospheric domain to data obtained in vacuum pulse response experiments is a bridging step across the pressure gap [4].

### References

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